

THE RELATION OF VAPOR PRESSURE TO PARTICLE SIZE

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The Thomson Equation

It has been shown on theoretical grounds that, if a liquid is broken up into small droplets, or if it is held in pores or other similar spaces which are of capillary dimensions, its vapor pressure is a function of the curvature of the surface¹ which is presented to the vapor phase. The relation between these quantities is set forth in the well-known Thomson equation;

$$(1) \quad \log_e \frac{P}{P_0} = \frac{2\gamma M}{rs RT},$$

where P and P_0 are the vapor pressures of a given liquid, respectively, at a surface whose radius of curvature is r and at a plane surface; γ is the surface tension of the liquid; T is the temperature on the absolute scale; M is its molecular weight; s is its density; and R is the gas constant.

The development of the Thomson equation is well known, and need not be repeated here. A typical treatment is given by Patrick.² It is an ideal expression, based upon fundamental thermodynamic principles. It is universally accepted, largely because of the weight of authority inherent in its source. But we have failed to find in the literature either any quantitative experimental confirmation of its predictions or any thorough study of its applicability and limitations. All the experimental evidence for it is of a purely qualitative nature; and, even as such, this evidence is not always clear and convincing.

Three assumptions are made in the development of the Thomson equation, namely:

A. The substance in the molecularly dispersed phase obeys the ideal gas laws.

B. The surface tension of the substance is independent of its degree of subdivision.

C. The density of the substance is independent of its degree of subdivision.

We have never yet found anything conforming exactly to the ideal gas laws, and so assumption A is assuming too much for the molecularly dispersed phase. For particles so large that the vapor pressure does not differ appreciably from that at a plane surface, only a negligible error is introduced; but when the molecular dimensions are approached the error will be large.

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¹ The curvature of a surface is equal to the reciprocal of its radius of curvature.

² "Treatise on Physical Chemistry." Edited by H. S. Taylor. Vol. II, p. 1290 (1925).

As to the second assumption, (B); it seems certain that the surface tension of a liquid must vary with its degree of dispersion. Sir William Thomson,¹ on the basis of the Laplace theory of surface tension, considered it probable that the surface tension of water at a meniscus whose radius of curvature is less than 0.0012 millimeter is no longer independent of the curvature of the surface, but his reasoning is not given. He cautions against using the equation for very small capillaries.

Freundlich,² upon a similar basis, reached the conclusion that the surface tension of a liquid in the form of small droplets must be less than that at larger surfaces. He believed this true for droplets whose radius is of the order of magnitude of the range of molecular action; but admitted that this does not give a satisfactory basis for the calculation of their size.

Patrick and Eberman³ found reason to believe, from studies of selective adsorption, that a liquid has a much higher surface tension than ordinarily if its surface is exceedingly concave, as it is when held in a very small capillary space. Other evidence is found in work by Patrick, Preston and Owens.⁴ They found that a gas will condense (presumably to a liquid) in the capillary spaces which are found in silica gel, at temperatures above its critical temperature. In other cases it was found that gases condensed in such capillary spaces at pressures which were always below the saturation pressures for these gases in contact with their liquid phases. They found, too, that adsorption takes place from solution above the critical solution temperature. It follows from these results that the critical temperature for a liquid in a capillary is higher than that for the liquid in bulk. If this is true, then the surface tension must also be higher, because the temperature—surface tension curve, which is nearly linear, cuts the temperature axis at or near the critical temperature.

Harkins, Davies and Clark,⁵ reasoning from the theory that molecules are oriented at interfaces, concluded that the surface tension of a liquid must be a function of the curvature of its surface. At a plane surface, or at one which is not greatly curved, the molecule can fit the surface; and under such conditions the normal surface tension is displayed. At a surface which is sufficiently curved, however, the molecules will be differently arranged. At such surfaces, then, the forces between them are modified, and a different surface tension should result.

The third assumption, (C), is also open to question. E. A. Fisher⁶ found that there is reason to believe that the density of water in a capillary pore is less than that of water in bulk. When a film is adsorbed upon a solid surface, he reasoned, it is held there by adhesive forces of great magnitude. If a very small capillary is partially filled with water the action of the forces which are

¹ Proc. Roy. Soc. Edinburgh, 7, 63 (1870).

² H. Freundlich: "Kapillarchemie," 63 (1922).

³ W. A. Patrick and N. F. Eberman: J. Phys. Chem., 29, 227 (1925).

⁴ W. A. Patrick, W. C. Preston and A. E. Owens: J. Phys. Chem., 29, 421 (1925).

⁵ W. D. Harkins, E. C. H. Davies and G. L. Clark: J. Am. Chem. Soc., 39, 592, 595 (1917).

⁶ E. A. Fisher: J. Phys. Chem., 28, 363-4 (1924).

active in its surface will tend to stretch the water in it. As a result it will be put under a tension, and its density will be reduced in proportion. He gives about three microns as the diameter of a capillary in which this effect would probably begin to be noticeable.

The assumptions upon which the Thomson equation is based are, then, somewhat unreliable. Like the equation itself, they stand in need of experimental investigation. In the absence of actual data it is impossible to make an exact statement, but the consensus of opinion seems to be that assumptions B and C fail to hold for a surface whose radius of curvature is of the order of magnitude of one micron, or less. This is approximately the limit of microscopic visibility. The Thomson equation is, then, from this point of view, applicable only to bodies which are experimentally measurable.

Calculations from the Equation

Calculation from the Thomson equation shows that the vapor pressure of a liquid at a curved surface differs from that at a plane surface by an amount which is quite inappreciable, even for droplets which are comparatively small. The values of the increase in vapor pressure, $P - P_0$, and of the relative increase in vapor pressure, $(P - P_0)/P_0$, as calculated for droplets of water and mercury of various sizes are given in Table I. Here P is the vapor pressure of the droplet, and P_0 is that at a plane surface. Thus the Thomson equation leads to the conclusion that the vapor pressure of a droplet of water or mercury exceeds that of a very large body of the same substance by one thousandth

TABLE I
Calculations from the Thomson Equation

Radius of droplet in centimeters	For Water		For Mercury	
	$P - P_0$ mm. Hg.	$\frac{P - P_0}{P_0}$	$P - P_0$ mm. Hg.	$\frac{P - P_0}{P_0}$
1.0	0.052	0.061	0.097	0.065
0.1	0.042	0.051	0.087	0.055
0.01	0.032	0.041	0.077	0.045
0.021	0.022	0.031	0.067	0.035
0.031	0.019	0.021	0.057	0.025
0.041	0.189	0.011	0.047	0.058
0.051	1.99	0.113	0.0399	0.764
0.061	33.84	1.930	0.036	28.094
0.071	818,710.	46,569.	5.6×10^{22}	4.35×10^{25}

of the latter value only when it has a radius of about one micron, i.e. 0.0001 centimeter. For surfaces of greater curvature the calculated effect increases, and becomes enormous for a droplet whose radius approaches the molecular dimensions.

The Thompson equation may be put in the form:

$$(2) \quad \log_e \frac{P}{P_0} = \frac{2\gamma M}{s RT} \cdot \frac{1}{r} = \frac{K}{r}$$

where K is a constant for a given liquid at a given temperature. Under

ordinary conditions K will always be very small, because the large value which must be assigned to R , the gas constant, will far outweigh the effect of the values of M , γ and s . We have calculated the values of K for eighty representative liquids at temperatures close to 20°C ., and find them to vary from 0.000,000,076 for methyl alcohol, a liquid of low molecular weight and low surface tension; to 0.000,000,56 for mercury, whose molecular weight and surface tension are the highest known. The average value of this constant for all these liquids is 0.000,000,25. It seems that its value for any liquid will lie between these limits. We may, then, say that K for any liquid at about this temperature is, for practical purposes, a constant, of the order of magnitude of 0.000,000,3. It thus appears that the vapor pressure of any liquid at a curved surface, as calculated from the Thomson equation, will differ from that at a plane surface by as much as one thousandth of the latter value, only when its radius of curvature is of the order of magnitude of one micron.

Theoretically, then, the Thomson equation should be applicable to surfaces whose radii of curvature are one micron or more in length. This lower limit is set by the probable limit of validity of the assumptions upon which the equation is based. A glance at Table I shows that the effect, in terms of vapor pressure, as predicted from the equation is very small for any droplet of water or of mercury such as would ordinarily be met with; so small, indeed, that it seems doubtful whether it could be effective at all. These considerations lead us to the conclusion that the limits within which the Thomson equation is actually applicable are probably very narrow.

The Thomson equation, with suitable modifications, holds quite as well, theoretically, for the vapor pressures of solid particles and for the solution pressures of solid or liquid particles as for the vapor pressures of liquid bodies.

Previous Experiments

The more important evidence for the Thomson equation may be briefly summarized. Numerous investigators have found that substances have greater solubilities when finely divided. A very pretty qualitative demonstration of this fact is due to Kenrick.¹ Ostwald² found that finely divided mercuric oxide is more soluble in normal solutions of potassium bromide and sodium thiosulfate than is coarser material. He got similar results for the solubilities of various salts in water. Hulett³ found that the solubility of gypsum and barium sulfate in water is greater when finely divided, and established the fact that, for particles of either substance larger than about two microns in diameter, the solubility is no longer a function of particle size. Both Ostwald and Hulett found that large particles grow slowly at the expense of very small ones when both are in contact with the same solution. No attempt was made to determine the solubility of the smaller particles as a function of particle size; so the experiments do not furnish any quantitative confirmation of the Thomson equation.

¹ F. B. Kenrick: *J. Phys. Chem.*, **16**, 516 (1912).

² Wilhelm Ostwald: *Z. physik. Chem.*, **18**, 159 (1895); **34**, 495 (1900).

³ G. A. Hulett: *Z. physik. Chem.*, **37**, 385 (1901); **47**, 357 (1904).

A number of investigators¹ have reported that larger crystalline bodies grow, by sublimation, at the expense of smaller ones. In all of these cases the details as to the conditions which prevailed during the experiments are meager or lacking. It seems to us probable that the changes noted were due to temperature differences rather than to differences in vapor pressure between the particles studied.

Ostwald² and McKeehan³ believed that, in certain systems, small droplets of liquids distil over to larger ones. We shall discuss these experiments in detail.

Other evidences of this sort might be cited, but the above will serve to indicate the nature and quality of the work which has been done.

Experimental Sulfur

Ostwald⁴, after discussing the difference in vapor pressure which exists between the surfaces of two droplets of unequal size, says:

"One can demonstrate the existence of such a difference by putting a liquid, which must not be too volatile, in a tube, evacuating and sealing it, and then producing a deposit of droplets on its walls. Now if the tube is put aside it will be found after some time that the droplets which were larger than the others at first have surrounded themselves with cleared spaces, showing that the neighboring smaller droplets have distilled over to these larger ones. A suitable material for this experiment is sulfur, which deposits from the vapor phase in the liquid form."

We repeated this experiment of Ostwald's.

Test tubes of soft glass were prepared by washing them with distilled water, allowing them to stand for 24 hours or longer filled with fresh aqua regia, steaming them out and drying them in an oven. The tubes were drawn out to provide a narrow neck for sealing off, and were then allowed to stay in the hot air bath until wanted. Our experience showed that tubes so prepared were satisfactorily clean.

Sulfur was at first prepared by distilling from a small retort, the distillate being run into conductivity water. After it had hardened it was dried and pulverized. Later, sulfur was prepared by recrystallizing from carefully purified carbon tetrachloride and drying in the hot air-bath for some hours.

A few fragments of sulfur were introduced into a tube which was then evacuated to some desired pressure and sealed. Gentle heating caused a deposit of sulfur droplets to form upon its walls.

Sulfur deposits from the vapor phase in liquid droplets which vary in size from those which can just be seen with a microscope to those which have

¹ W. D. Herman: *Chem. Centralblatt*, 1874, 3; J. Lawrence Smith: *Dingler's Polytechn. J.*, 121, 402 (1874); H. Freiherr Jüptner von Jonstorff: *Ber.*, 10, 866 (1877); O. D. von Engeln: *Am. J. Sci.*, (4) 40, 461 (1915); R. S. Willows and E. Hatschek: "Surface Tension and Surface Energy," 30 (1923).

² Wilhelm Ostwald: "Grundriss der allgem. Chemie," 96.

³ L. W. McKeehan: *Phys. Rev.*, (2) 8, 142-8 (1916).

⁴ Loc. cit.

a diameter of a millimeter or more. The nature of the deposit varies with the stage at which the deposition is stopped. Microphotographs of characteristic deposits are shown in Fig. 1. The droplets in light deposits are small, circular in cross section, and rather widely spaced. If the condensation of sulfur is slow and regular these droplets grow uniformly. After certain size is reached a process of coalescence sets in:—some droplets run together. An early stage in this process may be seen in A of Fig. 1. As condensation goes on, running together becomes more active; and it not uncommonly persists for some time after deposition of sulfur has been stopped. Droplet systems which have come to equilibrium, so far as this change is concerned, are very often like that shown in B; but it is possible to get systems whose droplets, though comparatively large, are very regular. After a time some of the larger droplets turn crystalline. A few which have so changed may be seen in B of Fig. 1.

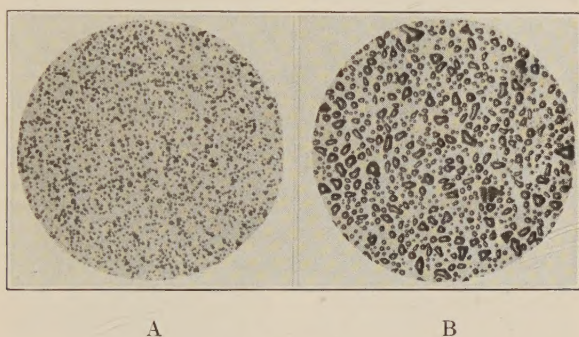


FIG. 1
Deposit of sulfur droplets
× 20

They are opaque, whereas droplets which are still liquid show axial spots of light. It seldom happens that more than a few droplets turn crystalline. The transformation is quite random, and apparently accidental. Constancy of temperature has a stabilizing effect, tending to prevent crystallization, and this effect is greater the higher the temperature.

The form of these droplets is significant. Some sulfur was deposited upon a small glass rod and examined under the microscope. As seen in vertical cross-section, the line of sight being tangent to the surface upon which they rested, the droplets were seen to be spread upon it, showing much flattened contours of the form which droplets of any liquid take when placed upon a surface which it wets. The deposit of sulfur upon glass is analogous to a thick film of oil upon water. We believe that the droplets of sulfur exist in more or less stable equilibrium with a thin film of liquid sulfur which covers all the rest of the glass surface and connects them all together, and that the existence of this film on the glass accounts for the manner in which the droplets run together.

We found that when these tubes with their droplet systems were set aside, cleared spaces formed just as described by Ostwald; but the central bodies to which distillation takes place are crystalline, not liquid.

Salomon¹ was apparently the first to observe the distillation of sulfur droplets to crystals. He found that, under the conditions of his experiments, crystals of nacreous sulfur are formed. Whitaker² describes, and shows by means of microphotographs, the formation of solid bodies of five types at the expense of sulfur droplets. These are: solidified droplets of indefinite form, octahedrons, nacreous plates, hexagonal plates and curved hair-like crystals. These forms were found with light deposits of fine droplets at atmospheric pressure. We have repeated this portion of his work with very similar results.

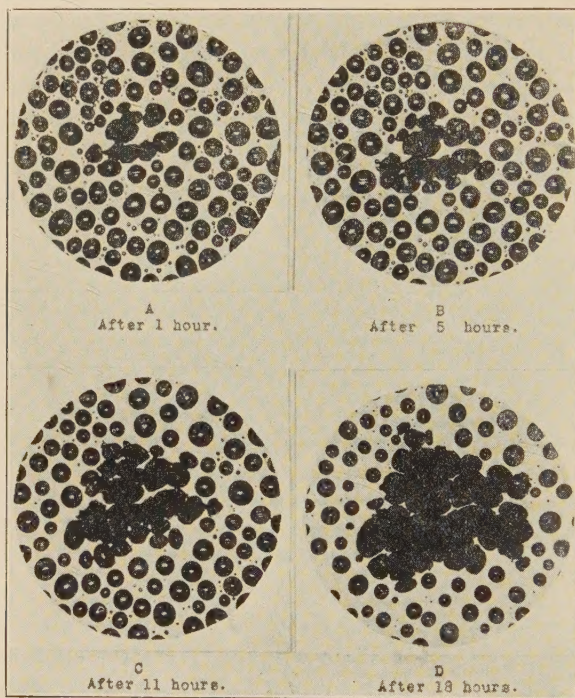


FIG. 2
Distillation of sulfur droplets to crystals. Room temperature.
× 50

The changes in a characteristic experiment of ours are shown in the microphotographs of Figs. 2 and 3. The pressure in this tube was 0.001 millimeter of mercury. It was kept at the temperature of the room. The deposit, which was very uniform, consisted of droplets which ranged from about 2 or 3 to 80 microns in diameter. Immediately after it was formed, the tube was brought under the microscope, and all parts of the deposit were examined. At the end of ten minutes a few widely scattered droplets had solidified. Our method was to select a small area for close study. We pasted a bit of paper with a hole in it on the tube in such a way that the chosen area was visible

¹ W. Salomon: *Z. Kryst. Min.*, 30, 605 (1899).

² H. Whitaker: *J. Phys. Chem.*, 29, 399 (1925).

through the hole. We found it convenient to refer to such a group of droplets as a system. In the system illustrated by the figures the droplet which is represented by the largest unit of the crystal aggregate shown in A was first to change over. The change then spread to neighboring droplets until the condition shown in photograph A was reached at the end of an hour. Thereafter the system was photographed at the intervals indicated. For more than ten hours the visible change consisted in the growth of the crystal aggregate by inclusion of more droplets. This change, due to coalescence, was at an end after 24 hours.

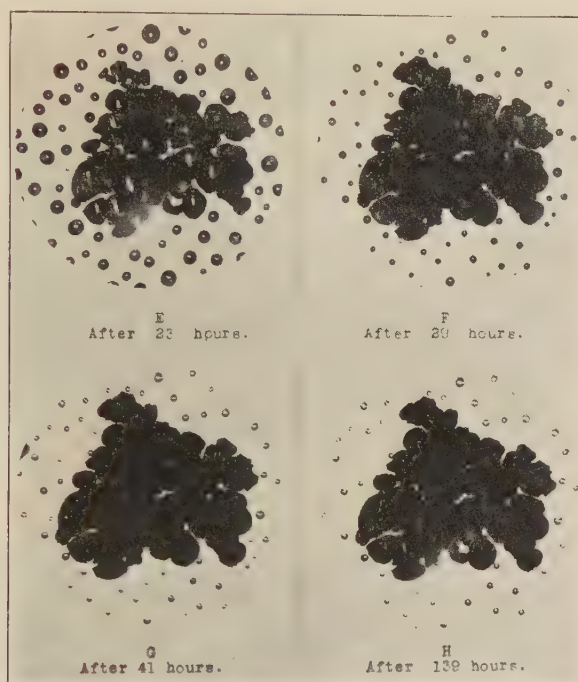


FIG. 3
Distillation of sulfur droplets to crystals, continued. Room temperature.
× 50

Distillation from the droplets to the crystalline aggregate was going on all the time, as is shown by the growth of the aggregate, but its effect in decreasing the sizes of droplets was definitely obvious only after 11 hours. Measurements of various droplets in succeeding photographs, beginning with photograph C, showed that all of them decreased in diameter at a rate which was roughly proportional to their respective sizes, so far as could be determined, regardless of size or position. After about thirty hours this decrease in diameter was at an end, and the further change consisted in the flattening of the droplets, as shown in F and G. At the end of four days more the condition shown in H was reached. The tube was kept for a month longer, but no further change was observed.

The distance across which distillation takes place from droplets to crystals is of interest. Our experiments indicate that it is definitely limited for given conditions. It was not possible to cover, in a single photograph, at this magnification, the whole area over which the change took place. Observation with the microscope showed that it was only a little larger than the area shown in the series of photographs after eighteen hours. It gradually extended until, after 41 hours it covered a roughly circular area with center at the middle of the crystal aggregate and radius about four millimeters. It was then encroaching upon the areas which were distilling to other centers. This, however, was about the limit which was reached, even after a month.



FIG. 4
Distillation of sulfur droplets to crystals. Room temperature.
× 20

In other cases we found no obvious coalescence and the droplets distilled completely away, leaving no trace. The changes in a typical experiment of this sort, again at room temperature and 0.001 millimeter pressure, are shown in Fig. 4. Even after a week the cleared spaces about the crystallizing aggregates were but little larger than those shown in the photograph which was taken after the expiration of seventeen hours.

It is noteworthy that, in a number of instances in this experiment, larger and smaller droplets were found very close together; yet no distillation took place from the latter to the former. Such a group is found at about the position which is 4 o'clock on the dial of a watch. Another is close to 3 o'clock, and yet another is between 8 and 9 o'clock. It seems that the distillation from droplets to crystals, with sulfur, is very much more rapid than the distillation between droplets of different sizes.

The spreading of the crystal state from those droplets which are first transformed to their immediate neighbors is evidently closely related to the running together of droplets which has been mentioned; for the droplet which undergoes the change is usually jerked toward the crystal aggregate which is already in existence at the instant when it is transformed. This feature of the change was observed many times under the microscope during our study of these systems. It was found sometimes, too, that a tiny tongue of solid sulfur connected the newly converted droplet with the original crystalline

mass. Several instances may be seen in A and B of Fig. 2. We believe that the crystalline state spreads to new droplets through the crystallization of a film of sulfur which lies on the glass between the droplets and the crystalline aggregates, and that the spreading ends when this film disappears by distillation. The running together of droplets, the spreading of crystallization and its cessation furnish very good evidence for the existence of such a film.

The changes described took place in the same manner, and at about the same rate at different pressures up to 12 millimeters of mercury. The presence of air at atmospheric pressure decreases the rate of distillation from droplets to crystals very greatly. So far as could be ascertained, constancy of temperature is not essential for the satisfactory progress of this distillation. Under the most favorable conditions, however, the distillation is very slow at low temperatures.



FIG. 5
Distillation of sulfur droplets to crystals. 75°C .
 $\times 40$

Experiments were tried at higher temperatures also. It was found that when evacuated tubes were placed in a hot air bath at approximately 75°C . the sulfur droplets in them distilled rather rapidly from place to place, due to temperature differences, thus preventing the study of the distillation from droplets to crystals which is produced by vapor pressure differences.

Experiments at higher temperatures with tubes which contained air at atmospheric pressure were more successful. In these experiments the tubes were inserted in the hot air bath for five minutes, removed for examination and photographing and then again returned to the bath. Microphotographs from one such experiment are shown in Fig. 5. Apart from the more rapid clearing away of droplets, which was obvious, it is noteworthy that spreading of the crystalline state to new droplets was practically eliminated.

We next suspended the tubes with their systems in the vapors of boiling chloroform, carbon tetrachloride, and toluene, respectively, in large test tubes, and observed them where they were, using a low-powered microscope mounted upon a cathetometer. This eliminated the necessity of removing the tubes for examination. There was no distillation due to temperature differences. We found, as anyone would expect, that the changes are more rapid and more extensive the higher the temperature and the lower the pressure.

There was, however, no regularity either in the rate in which given droplets decreased in size or in the rate at which cleared spaces extended about growing crystals. This is, no doubt, due to the fact that not one, but always several crystals were growing simultaneously, and the changes were correspondingly complex.

All this, however, failed to settle the question whether large liquid droplets of sulfur grow at the expense of smaller ones by distillation, or not. We found that if a tube was put into the vapor of a boiling liquid in one of our "test tube" thermostats at 60° C. or higher, immediately after a deposit had been formed in it and before any of its droplets had a chance to turn crystalline; all its droplets remained liquid indefinitely. Under these conditions, no cleared spaces were found to form in experiments which lasted as long as three weeks.

Crystals such as formed in many experiments, when melted, give droplets which are sometimes three millimeters or more in diameter, and these droplets also remain liquid indefinitely if kept at a constant temperature of 60° C. or higher.

Systems were now prepared by melting such crystals, and then quickly causing a little sulfur to deposit around the droplet which had just formed. The tubes were then put in the thermostat, generally in the vapor of boiling chloroform, and watched by means of a low power microscope. In no case did we find any clearing of spaces about the large droplets, or any other indication of a distillation of sulfur from small droplets to large ones, even in experiments in which the observations were continued through three weeks. In these experiments the large droplets were .3 to .7; and the small ones were 0.001 to 0.030 millimeters in diameter.

Since we have never found distillation from small droplets of liquid sulfur to large ones under any conditions, it seems fairly certain that Ostwald was in error in believing that he had observed it. What he saw was undoubtedly the distillation from droplets to crystals. The getting of data upon the relation of vapor pressure to particle size is manifestly impossible with these systems.

Phosphorus and other Substances

A number of experiments which we have performed show that yellow phosphorus behaves, in general, in exactly the same manner as does sulfur. It deposits from the vapor phase in droplets; these droplets coalesce by running together; some of them turn crystalline after a time, and when they do the crystalline state spreads to neighboring droplets; and droplets distil to crystals or to crystalline aggregates. Some experiments which we performed in a thermostat at 61° C. showed that, under these conditions, small droplets do not distil over to the larger ones in the course of a week. We believe that liquid phosphorus, like liquid sulfur, wets glass; and that when deposited on glass its droplets have practically the same vapor pressure regardless of size.

We have carried out numerous experiments with water, ether, carbon disulfide, chloroform, carbon tetrachloride, toluene, nitrobenzene, anilin,

and acetic acid deposited upon glass. When the tubes containing such deposits are exposed to the air of the room distillation due to temperature differences always takes place. When, however, they are kept in a carefully regulated thermostat this distillation ceases. Running together of the droplets occurs readily and irregularly. We were unable to obtain anything like the clear-cut "systems" which we had with sulfur and phosphorus. These experiments did not lead us to anything new; but they certainly did not furnish any evidence that vapor pressure is a function of particle size for droplets of these liquids upon glass.

We conclude, contrary to the generally accepted belief, that droplets of liquids which wet glass, when deposited upon it, do not show the distillation from small droplets to large which is predicted from the Thomson equation.

Mercury

McKeehan¹ found that small droplets of mercury distil to large ones provided the space above them is enclosed so that it becomes saturated with mercury vapor.

Mercury droplets upon glass are practically spherical in form, provided they are less than about one millimeter in diameter. The deposits show no tendency to run together. So great is the inertia of the droplets, due to the high density of mercury, that they are rather easily displaced by jarring unless they are very small. When so brought into contact, they of course, unite; but the process is not at all like that which found is with liquids which wet glass, either in its progress or in the nature of the bodies which result from the union. Only reasonable care in handling is sufficient to avoid moving the droplets if none of them are larger than one millimeter in diameter.

The mercury which we used in these experiments was given a preliminary purification by dropping it through a long tube filled with 10% nitric acid. This product was then twice distilled by the method of Hulett², aspirating air through it at a pressure of 25 millimeters of mercury. When wanted for use it was drawn from beneath the surface by means of the device commonly employed in a wash-bottle. That which first came from the delivery tube was always rejected to avoid contaminations.

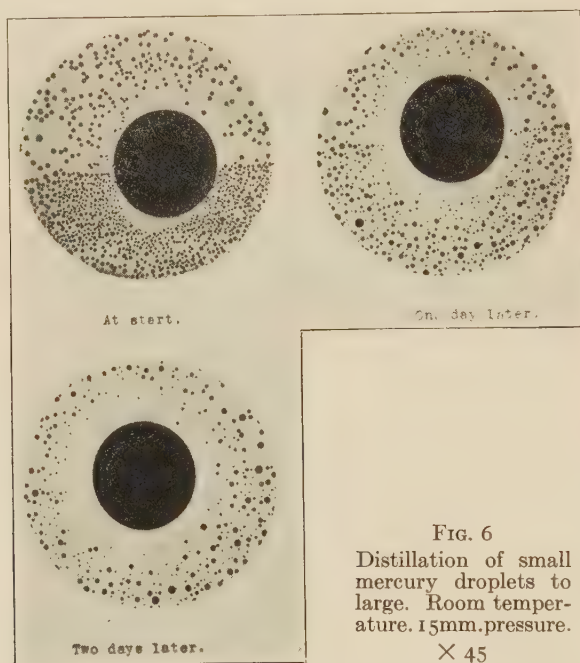
Preliminary experiments showed that the droplets of a deposit formed from the vapor phase upon the walls of a tube are either uniform in size, or show a uniform graduation from large to small as the distance from the place where the mercury is distilled increases. In either case there is little change in such deposits over a period of a week or more. What is needed for the experiment is a system in which large and small droplets lie very close together. After some trials we worked out the following method by which such systems may be prepared. A small droplet of mercury is introduced into one of the prepared tubes, which is then evacuated and sealed. The tube is then immediately reversed so that the mercury in it is brought in contact with the hot end. It distills with such violence that it is disrupted into small particles

¹ Loc. cit.

² G. A. Hulett: *Phys. Rev.*, (1) **21**, 388 (1905).

which fly about in the tube. Where these particles strike the walls they, adhere. In their flight they emit mercury vapor, which then deposits in fine droplets. It is usually possible to find in a tube a few systems in which small droplets lie very close to others many times their size, after this process.

In the first experiments the tubes were suspended in the air of the room between observations. Fig. 6 shows the changes which took place in one ex-



periment, which was typical of very many. The large droplet had a diameter of about 300 microns. At the end of 24 hours, as may be seen, the droplets to a distance of about 0.1 millimeter from the large one had decreased in size, and many of those which were closest had quite disappeared. It is noteworthy that beyond this distance the larger ones among the small droplets had grown at the expense of those which were still smaller. At the end of another 24 hours the clearing away of small droplets around the larger one was more nearly complete, though the space affected was but little greater. The closer small droplets which had grown during the first 24 hour period had decreased somewhat at the end of the second. Those which lay still farther out, however, had continued to grow. The next microphotograph, taken after another 24 hours, showed very little further change. After this time the process was apparently at an end, and observations were discontinued after a week.

The tube in the experiment just described was sealed at a pressure of 15 millimeters of mercury. Although there was some irregularity in the rate of distillation, in a number of experiments at lower pressures the clearing away of small droplets was found to be more rapid and more exten-

sive the lower the pressure. In every case it was found that the larger droplets among the small ones tend to grow at the expense of their smaller neighbors. At the lowest pressure, 0.001 millimeter of mercury, the cleared space extended to a distance of about 0.2 millimeters from the large droplet at the end of two days. In general, the clearing away of droplets was apparent at the end of an hour or two; it continued at a decreasing rate for two to four days, and then it came to an end. We have kept many tubes for as long as a month, and some for as long as two years; but we have failed to find any noteworthy change after four days. In some tubes sealed at atmospheric pressure we have found that practically no change at all takes place, even during the first few hours.

It is surprising, if a difference of vapor pressure due to a difference in size exists in these systems (and the experiments show that it does, at least at first) that all the smaller droplets do not distil completely away to the larger, regardless of their position. The fact remains that they do not, nor have we ever been able to bring about such a result, in spite of the most scrupulous care in purifying the mercury and in cleaning the tubes. We believe that the main difficulty is due to a contamination or alteration of the surfaces of the droplets which progressively slows down and finally stops their distillation.

Many experiments were carried out as above, except that the tubes were fastened vertically in a thermostat at 25° C. when they were not being examined. The changes were not appreciably more regular, or different in rate, at constant temperature.

It was found in some experiments that when a tube with mercury droplets deposited throughout the length of its walls is fastened vertically in a thermostat at constant temperature there is a tendency for the mercury to distil from above downward. This is, of course, due to the fact that in such a system the pressure of the vapor falls off with increasing height. Attempts were made to study the rate of distillation of the droplets as a function of their distance above the bottom of the tube. We found that the changes which the droplets underwent were so irregular that no correlation of rate of distillation with height was possible. We attribute these irregularities to contaminations of, or change in, the droplet surfaces.

This distillation due to difference in height interferes with the distillation from small droplets to large when the tubes are kept stationary, as in all the experiments hitherto described. Accordingly, we fastened our tubes upon the arms of a rotator which revolved in a vertical plane in the thermostat. This device served also to eliminate any temperature differences which might exist between different parts of the tube. Further experiments in highly evacuated tubes with this modification showed more regularity in the outline of the cleared spaces around the largest droplets, perhaps, but there was no other new feature.

We measured the changes which certain droplets suffered in given times in the hope of discovering some law governing this change. Five series of microphotographs of as many systems, taken at intervals of 12 hours, were prepared; and the images of four selected droplets, as close to the large

droplet of each system as possible were measured with a filar micrometer on each of four negatives from each series. It was found that the changes in diameter with time were very irregular. In the twenty series there was no recognizable uniformity of behavior, even in a general way. The centers of distillation and of condensation in such systems as these are so numerous that analysis of their mutual effects presents hopeless difficulties.

It was evident that simpler systems must be prepared if any regularity was to be discovered. After some trials the following method of getting such simpler systems was worked out. A fairly large droplet of mercury was introduced into a clean dry tube which had been provided at its closed end with a small bulb which could be sealed off later. After evacuating to 0.001 millimeter or less, and sealing and cooling the tube, it was held in one hand and struck sharply against the palm of the other. The mercury was thus broken up and its particles were projected to different parts of the tube, where they adhered to its walls. In many cases systems were formed in which several small droplets were very close to a large one. In case of failure, the excess mercury was used to sweep up all the droplets and the operation was repeated.

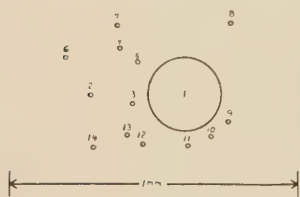


Fig. 7
Sketch of droplet system.

When a satisfactory system had been prepared, all other droplets were swept up, and the waste mercury run into the bulb prepared for it, which was then sealed off and rejected. The system was sketched as seen under the microscope, and a number was assigned to each droplet. They were then carefully measured with a filar micrometer and the mean of several determinations of different diameters was recorded. The tubes were rotated in the thermostat at 25° C. between measurements, which were made at varying intervals.

The results in one of the best of the experiments performed are shown in Table II. Fig. 7 shows the sketch of the corresponding system. As will be seen, the changes were hardly outside the limits of accuracy of the measurements which were made. Such experiments are almost wholly inconclusive.

We have succeeded in getting a very few systems in which one or two droplets about ten microns in diameter lay within 0.1 millimeter of large droplets. Careful studies of them after the manner described above showed that the small droplets scarcely decreased at all in diameter in a time as long as 60 hours.

In view of the slowness of the distillation from small droplets to large with mercury, and of the irregularities of the process, due presumably to surface changes, we are forced to conclude that numerical data upon the relation of vapor pressure to particle size cannot be had from experiments with them.

We were at first, completely at a loss to explain just why small droplets of liquids which wet glass do not distil over to larger ones, while the phenomenon is found with mercury, which does not wet glass, or wets it in less degree. A part of the explanation, it seems, may lie in the fact that droplets of wetting

liquids are very much flattened, and so do not have great curvature even when very small. We believe, however, that the real explanation lies in the nature of the deposits. If droplets of a liquid upon a surface which it wets are in equilibrium with a film of the liquid which is spread upon the surface between them, it follows from the definition of equilibrium that they have the same vapor pressure as does the liquid in the film, and so the vapor pressure of all the droplets is the same. It is not to be expected, then, that there will be any distillation from certain droplets to others unless some such influence as a difference in temperature brings it about.

TABLE II

The rate of distillation of small mercury droplets to large.
Diameters in millimeters at elapsed time:

Time in hours	0	26	55
Droplet 1	0.253	0.254	0.254
2	0.014	0.018	0.016
3	0.010	0.010	0.007
4	0.010	0.010	0.009
5	0.017	0.017	0.020
6	0.015	0.015	0.018
7	0.011	0.013	0.013
8	0.013	0.013	0.009
9	0.012	0.011	0.007
10	0.014	0.013	0.010
11	0.012	0.012	0.007
12	0.010	0.006	0.005
13	0.013	0.012	0.011
14	0.012	0.006	0.005

Crystals of Iodine and other Substances

No experiments have been more widely quoted in support of the Thomson equation than those having to do with the growth of large crystals at the expense of small ones by sublimation. We, too, have found instances of the growth of certain crystals at the expense of others by sublimation; but always under such circumstances that we were led to believe that differences of temperature were the most important, if not the only active cause. It seemed from our other work that, at constant temperature, sublimation should occur only very slowly and over very small distances between crystals of different sizes.

When iodine is heated rapidly in a closed system it may be made to melt *in situ*, and when it solidifies again the crystals which form adhere well to the surface on which they rest. Rather irregular crystal masses may be formed in this way. When the iodine which has been driven to other parts of the tube is now gently sublimed to the neighborhood of the larger crystals, this area being cooled by applying a wet cloth, systems consisting of large crystals closely surrounded by small ones are formed.

Three such systems were prepared in tubes which had been evacuated to a pressure of about one millimeter. It was found that the large crystals were 1 to 3.5 millimeters, while the smaller ones were close to 0.1 millimeter in greatest dimension. We have not succeeded in getting smaller crystals than this by sublimation. These tubes were rotated in the thermostat at 25° C. for a month, and removed and examined under the microscope at intervals. The small crystals were not cleared away from around the large ones, nor did they decrease appreciably in size during this time.

Experiments were carried out with very similar systems of iodine crystals in the "test tube" thermostat at the boiling point of chloroform, examining the crystals from time to time with a low power microscope without removing them from the bath. In these experiments, which lasted from eight to nine days, there was no clearing of spaces around the large crystals. No decrease in the size of the small crystals was detected.

Similar experiments with naphthalene and camphor were unsuccessful in that no distillation from small particles to large was found.

These experiments show that the difference in vapor pressure which is due to a difference in particle size must be negligibly small for crystals, unless some of them are very small indeed. For crystals of macroscopic size it must be practically non-existent. Yet these systems, which failed to show any change in constant temperature, never failed to show sublimation from one part of the tube to another when left for a few hours in contact with the air of the room, with its slight temperature differences.

Small and Large Meniscus

Another method by which it seemed that quantitative data might possibly be secured upon the relation between vapor pressure and particle size, or size of meniscus, was suggested by an experiment of Washburn.¹ He suspended a small capsule partially filled with water over water in a large vessel; and found that, at constant temperature, water distilled from the capsule down to the large surface. When he suspended the capsule with its liquid well below the level of the large surface, he found that water distilled from the large surface to the water in the capsule. Obviously, if the meniscus of water in the capsule had been brought to the proper level, so that the vapor pressure at its surface was equal to that at the large surface less the pressure of the column of vapor between these two levels, no distillation at all would have taken place. The pressure of the vapor in a system at any point above or below a plane surface may be calculated by means of a well known equation.² If, then, we can determine experimentally the height at which a small meniscus must be above a large surface to be in equilibrium with its adjacent vapor and neither gain nor lose liquid, we can calculate the vapor pressure. The practical applicability of the method will be determined by the rate at which distillation takes place to or from the small meniscus when near its equilibrium position.

¹ E. W. Washburn: *J. Am. Ceramic Soc.*, **1**, 25 (1918).

² J. W. Mellor: "Higher Mathematics for Students of Chemistry and Physics," 61 (1922).

We prepared an apparatus in the form of an inverted U tube with large and small arms, as shown in Fig. 8. The arms had radii, respectively, of about 8 and about 1.5 millimeters. After cleaning and drying, the apparatus was filled nearly full of liquid. It was then evacuated, the liquid was boiled gently to ensure the expulsion of all air, and then it was sealed. The meniscus was brought to the desired position in the smaller tube, (the disposition of the meniscus in each tube was much as shown in the figure in every case), and the apparatus was completely immersed in the thermostat bath. After about two hours had been allowed for the liquid to drain from the walls, measurements were started. Thereafter the position of the small meniscus was determined from time to time with reference to a mark on the small tube, using a cathetometer with micrometer slide attachment which read to 0.001 millimeter.

In experiments at 20° C. toluene and benzene showed no change in twelve hours. Water showed a very slight rise. Ether showed a rise of about 0.012 millimeters in that time. At 40° the rates for ether and water were somewhat more than doubled. At 50° the rates for both liquids were again somewhat more than doubled. Ether showed a rise of about 0.06 millimeters per hour at this temperature. These rates are very low, in spite of the fact that the surfaces were disposed so as to favor the distillation. With smaller capillary tubes we found the effect to diminish progressively, until tubes of radius about 0.4 millimeters were reached. These smallest tubes showed no effect at all, even with ether, during a period of several days.

This experiment was first proposed in a somewhat different form in Sir William Thomson's original article. It was actually tried by Bacon¹, who found that, in one year, less than 0.056 grams of ether has been transferred into a capillary tube in which ether originally stood at about the same relative distance below the large surface as in our experiments.

It is evident from these experiments that a meniscus, near its equilibrium position, would rise or fall at a rate much too slow for measurement. The actual determination of the equilibrium position for such a meniscus seems impossible.

We made other experiments with a drop of benzene about two millimeters in diameter suspended from a ring of platinum wire about one centimeter above a large surface of benzene. The containing vessel was thoroughly exhausted before sealing. We kept it immersed in the water of a thermostat at 25° C. and the droplet was observed from time to time through a low power microscope. No change in the droplet could be certainly detected short of 24 hours, and a week was required for it to disappear. A very much smaller droplet suspended from a fine platinum wire in a similar apparatus under the same conditions disappeared only after the expiration of three days. This confirmed



FIG. 8

¹ A. A. Bacon: Phys. Rev., (1) 20, 1 (1905).

our belief that distillation due to a difference in height is very slow. We concluded that we could not get quantitative experimental confirmation of the Thomson equation by experiments of this type.

Summary and Conclusion

Theoretical considerations have been given which lead us to the belief that the limits within which the Thomson equation is actually applicable must be very narrow.

Ostwald's experiment with sulfur droplets, wherein clear zones appear surrounding larger particles, is one of the most generally cited illustrations of the application of the Thomson equation. But we have found that whenever clear zones appear the central particle is solid. If all droplets are kept liquid no measurable distillation occurs. We have demonstrated this with sulfur and phosphorus and other liquids which wet glass.

We have found evidence which supports the conclusion that a liquid upon a surface which it wets forms droplets, in equilibrium with a film of liquid on the solid between them; a system analogous to that formed by an oil film on water or mercury. We believe that small droplets of wetting liquids, on glass, do not distil to larger ones because they form such systems.

With mercury, which either does not wet glass or wets it less than the substances above named, we found that larger globules grow at the expense of smaller, as have other observers. This is qualitative evidence in favor of the equation; but we found it impossible to secure data which would serve for a quantitative test. This distillation stops after the lapse of a few days in a singular fashion, explainable perhaps as due to contamination, perhaps to orientation of molecules in the surfaces.

We were unable to detect growth of larger crystals at the expense of smaller ones with such substances as iodine, naphthalene and camphor.

We found distillation between a large and a small liquid meniscus to be so slow that it would be useless to attempt to determine experimentally the equilibrium position of any meniscus, with reference to a large surface of the same liquid.

Persistent efforts extending over several years have failed to yield any quantitative experimental data supporting the Thomson equation. We conclude that the causes and effects formulated by that equation are so small that they are usually obscured or obliterated by other causes and effects always simultaneously present. Therefore it is not justifiable to refer to it as an explanation of phenomena so generally as is now the custom.

We do not presume to question any step in the logical thermodynamic reasoning leading to the Thomson equation. Indeed it was our faith in the accuracy of that reasoning which led us to hope so long that we should ultimately be successful in obtaining experimental confirmation. But our experience leads us to question the usefulness of the equation, either in explanations or in predictions.

